

# CATALYTIC HYDRODESULFURIZATION OF BITUMEN

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## ABSTRACT

Investigations of the catalytic hydrodesulfurization of Venezuela bitumen and its water emulsion (Orimulsion) were carried out. This material contained a large amount of sulfur and organometallics, such as vanadium and nickel compounds. A variety of nickel and molybdenum catalysts were prepared. These, as well as two commercial catalysts, were tested with Orimulsion and vacuum-dried, pentane-insoluble and -soluble bitumen. Catalytic hydrotreatment removed up to 75% of sulfur from the bitumen. Hydrodesulfurization was found to be affected by reaction temperature, reaction time, catalyst, and feed material. Moisture-free bitumen and a pentane-soluble bitumen fraction were desulfurized more effectively than Orimulsion. Zeolite-based catalysts gave higher desulfurization than synthetic clay catalysts.

## INTRODUCTION

The sulfur content of many coals, crude oils, and bitumens results in serious problems in the utilization and processing of these resources, both as fuel and nonfuel materials. Emission regulations demand that cleaner fuels be utilized. The production of low-sulfur, low-metal petroleum coke (petcoke) is also being sought for the manufacture of needle cokes, carbon electrodes, metallurgical reductions, and fuels. Unfortunately, the feedstocks available for production of fuels and carbon products tend to have higher sulfur contents, e.g., the very large reserves of crude oil and bitumens that are available in South America with sulfur contents of greater than 3 wt%. Lower-value sour crudes are also an increasing problem for oil production in parts of the United States.

Previous work at the Energy & Environmental Research Center (EERC) was concerned with the development of catalysts for production and upgrading of coal liquids, including hydrodesulfurization. The types of catalysts investigated included zinc chloride-silica complexes (1), metal-impregnated natural and synthetic clays (2-5), and zeolites (5). Molybdenum sulfide impregnated in a nickel-substituted synthetic mica montmorillonite (NiSMM) and in a hydrotalcite clay were demonstrated to be highly effective catalysts for hydrodesulfurization of coal-derived products.

Further demonstrations of the activities and stability of these catalysts for desulfurization of petroleum resids and bitumens are needed. Currently used resid desulfurization catalysts experience severe deactivation as a result of plugging of the catalyst pores or sintering of the metal sulfides. Several catalysts that previously exhibited activity for hydrodesulfurization of coal-derived materials were tested for desulfurization of a Venezuela bitumen. This material is marketed as a water emulsion product called Orimulsion.

## EXPERIMENTAL

The hydrodesulfurization tests were conducted in a small batch reactor with hydrogen pressures of about 1000 psi at a temperature of 390°C. The emulsion form (a 70% bitumen-30% water emulsion) is convenient for weighing and transferring the bitumen, and therefore the emulsion as well as the moisture-free bitumen (71 wt%) obtained by drying the water emulsion were used in tests. The moisture-free bitumen was further fractionated into pentane-soluble (83 %) and pentane-insoluble (17 %) fractions.

### *Catalysts*

Catalysts used in this study included the following: 1) chromia-pillared clay + molybdenum (6), NiSMM + molybdenum (7, 8), 2) Y-Zeolite + nickel-molybdenum (9), 3) Y-Zeolite + nickel-tungsten (9), 4) Y-Zeolite-aluminosilicate (10) + nickel-molybdenum, 5) Hydrotalcite + molybdenum (4), 6) uranium oxide-nickel oxide (11), 7) uranium oxide-nickel oxide + molybdenum prepared by impregnation of above catalyst, 8) AMOCAT and HDN-30.

### *Catalytic Reactions*

The catalysts were presulfided by heating with elemental sulfur plus hydrogen (200 psig) at 400°C for 2 hr. In a typical experiment, 1.50 g of Orimulsion or 1.0 g of dry bitumen or 1.0 g of pentane-soluble fraction and 0.5 g of the catalyst were placed in a tubing bomb (15-mL microreactor). The microreactor was evacuated, pressurized with 1000 psig of hydrogen, and placed in a rocking autoclave heated to the desired temperature. Heating was continued for 1 or 3 hours. At the end of the reaction period, the microreactor was cooled to room temperature, degassed, and opened. The product slurry was extracted

with tetrahydrofuran, and the solid catalyst removed by centrifugation. The supernatant liquid was evaporated to remove solvent, and the dried product was analyzed for sulfur. Total sulfur determinations were done with a LECO Model 532 sulfur analyzer using the American Society for Testing and Materials (ASTM) D1551 method.

## RESULTS AND DISCUSSION

### *Synthetic and Pillared Clay-Supported Molybdenum*

In a 1-hr test with the as-received emulsion (Orimulsion), the synthetic clay-supported molybdenum catalyst (NiSMM + 5% molybdenum, presulfided) gave a product with 3.0% sulfur (dry basis), which is a 23% reduction in the sulfur content of the bitumen (Table 1). Minimal hydrocracking and gas formation occurred under these conditions, although it is likely that some asphaltene hydrogenation occurred. The viscosity was not significantly changed.

A chromia-pillared clay containing impregnated molybdenum (molybdenum-high-chromium-pillared clay [Mo-HCPC]) was presulfided, and the catalyst was tested for hydrodesulfurization activity with the Orimulsion (Table 1). This catalyst exhibited a similar poor desulfurization activity (10% sulfur reduction).

The reaction of Orimulsion with the molybdenum sulfide-impregnated hydrotalcite (MoHT) catalyst gave a product with 3.6% sulfur (8% reduction) (Table 1). This catalyst gave respectable desulfurization with coal-derived liquids as well as model compounds (4), but apparently it is hindered by the aliphatic content of the bitumen, which may inhibit diffusion into the small pores of the catalyst.

### *Commercial Catalysts*

The presulfided commercial molybdenum catalysts, AMOCAT and HDN-30, both removed 39% of the sulfur of the Orimulsion (dry weight basis) in the 1-hr batch hydrodesulfurization test (Table 1). On this basis, we concluded that the EERC catalysts that previously showed desulfurization activities with coal liquids were far inferior to the commercial catalysts for desulfurization of the highly aliphatic bitumen. The form of sulfur present in the bitumen is likely to be partly heterocyclic as it is in the coal, but the matrix is entirely different in the bitumen.

### *Y-Zeolite-Supported Catalysts*

Further catalyst screening was carried out with zeolite catalysts modified by metal impregnation and also by coating the zeolite with aluminosilicate (cogel) as is done with fluid catalytic cracking (FCC) refining catalysts. The zeolite-supported nickel-molybdenum catalyst gave a 32% reduction of sulfur, and a similar zeolite-supported nickel-tungsten catalyst gave only a 22% sulfur reduction in 1-hr tests (Table 1).

More encouraging results were obtained with the catalyst prepared by impregnating nickel and molybdenum into a zeolite-aluminosilicate cogel (Table 2). The cogel-supported nickel-molybdenum catalyst gave 43% removal of sulfur in a 1-hr test. This catalyst is similar to that recently reported by a Canadian group (12). Further testing with Orimulsion for 3 hours gave 58% removal. When a dry fraction of the bitumen was hydrotreated with this catalyst for 3 hours, 37% of the sulfur was removed. Similar reaction with a pentane-soluble fraction of the bitumen resulted in 74% sulfur removal to give a product with 1.0% (dry weight basis) sulfur content. However, when the same reaction was carried out using 10 wt % of the catalyst, only 25% sulfur was removed.

### *Mixed Oxide Catalysts*

Good results were also obtained with a nickel catalyst supported on uranium oxide, which gave 38% removal of sulfur from the as-received Orimulsion in the 1-hr period (Table 3). The function of the uranium oxide is to prevent sintering of the nickel during regeneration of the catalyst. A hydrodesulfurization reaction of the moisture-free bitumen with this catalyst for 3 hours gave the same reduction in sulfur as that obtained with the Orimulsion. Thus with this catalyst, the water present in the emulsion does not appear to interfere with the reaction. Impregnation of molybdenum (5%) into this nickel catalyst resulted in a slight increase in catalytic activity (41% sulfur reduction). Better desulfurization was expected for this catalyst, but since far superior results were obtained with the zeolite catalyst, further work with the molybdenum-nickel-uranium oxide catalyst was suspended.

## CONCLUSIONS

Two catalysts that had previously exhibited activity for hydrocracking coal tar constituents were active for hydrodesulfurization of the high-sulfur Venezuelan bitumen. The most active catalyst for hydrodesulfurization was a nickel- and molybdenum-impregnated Y-zeolite-aluminosilicate cogel. This catalyst removed 75% of the sulfur from the moisture-free bitumen and 58% of the sulfur from the Orimulsion. A nickel-molybdenum catalyst supported on uranium oxide gave slightly better results than

desulfurization with the commercial catalysts. Other catalysts that had exhibited activity for desulfurization of coal-derived liquids were less active for desulfurization of the bitumen than the commercial hydrotreating catalysts.

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. Sharma, R.K.; Diehl, J.W.; Olson, E.S. "Hydrodesulfurization with a New Solid Acid Catalyst," In *Processing and Utilization of High-Sulfur Coals III*; Markuszewski, R.; Wheelock, T.D., Eds.; Elsevier: Amsterdam, 1990; pp 735-743.
2. Olson, E.S.; Buchwitz, C.M.; Yagelowich, M.; Sharma, R.K. *Prepr. Pap.—Am. Chem. Soc., Div. of Fuel Chem.* **1993**, *38*, 156-162.
3. Olson, E.S.; Yagelowich, M.C.; Sharma, R.K. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1992**, *37*, 262-267.
4. Sharma, R.K.; Olson, E.S. "Catalytic Hydrodesulfurization with Hydrotalcites," In *Processing and Utilization of High-Sulfur Coals IV*; Dugan, P.R.; Quigley, D.R.; Attia, Y.A., Eds.; Elsevier: Amsterdam, 1991; pp 377-384.
5. Olson, E.S.; Sharma, R.K. "New Catalysts for Production of Synthetic Fuels," In Proceedings of the Australian/U.S.A. Workshop on Low-Rank Coals, Billings, MT, May 23-24, 1991; EERC publication.
6. Sharma, R.K.; Olson, E.S. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1994**, *39* (3), 702.
7. Heinerman, J.J.L.; Freriks, I.L.C.; Graaf, J.; Pott, G.T.; Coglegem, J.G.F. *J. of Catal.* **1983**, *80*, 145.
8. Olson, E.S.; Sharma, R.K. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1994**, *39* (3), 706.
9. Haynes, H. W., Jr. *Ind. Eng. Chem. Process. Des. Dev.* **1983**, *22*, 401.
10. Pecorara, T.A. U.S. Patent 5 001 097, 1991.
11. Berry, F.J.; Murray, A.; Parkyns, N.D. *Appl. Catal. A* **1993**, *100*, 131.
12. Diaz-Real, R.A.; Mann, R.S.; Sambhi, I.S. *Ind. Eng. Chem. Res.* **1993**, *32*, 1354.

Table 1. Hydrodesulfurization Reactions of Bitumen

| Catalyst       | Substrate  | Subst.: Cat.<br>Ratio <sup>a</sup> | Time,<br>hr | Sulfur in<br>Substrate, <sup>b</sup> % | Sulfur in<br>Product, % | Sulfur<br>Removed, % |
|----------------|------------|------------------------------------|-------------|--|-------------------------|----------------------|
| Mo-NiSMM       | Orimulsion | 2                                  | 1           | 3.9                                    | 3.0                     | 23                   |
| Mo-HCPC        | Orimulsion | 2                                  | 1           | 3.9                                    | 3.5                     | 10                   |
| NiMo-Y-Zeolite | Orimulsion | 2                                  | 1           | 3.9                                    | 2.7                     | 32                   |
| NiW-Y-Zeolite  | Orimulsion | 2                                  | 1           | 3.9                                    | 3.0                     | 22                   |
| MoHT           | Orimulsion | 2                                  | 1           | 3.9                                    | 3.6                     | 8                    |
| AMOCAT         | Orimulsion | 2                                  | 1           | 3.9                                    | 2.3                     | 39                   |
| HDN-30         | Orimulsion | 2                                  | 1           | 3.9                                    | 2.4                     | 39                   |

<sup>a</sup> Ratio is based on the dry weight of bitumen contained in the Orimulsion.<sup>b</sup> Percent sulfur is based on the dry weight of bitumen contained in the Orimulsion.

Table 2. Hydrodesulfurization Reactions of Bitumen with NiMo-Y-Zeolite-Aluminosilicate Cogel

| Substrate       | Substrate: Cat.<br>Ratio | Time,<br>hr | Sulfur in<br>Substrate, <sup>a</sup> % | Sulfur in<br>Product, % | Sulfur<br>Removed, % |
|-----------------|--------------------------|-------------|--|-------------------------|----------------------|
| Orimulsion      | 2 <sup>b</sup>           |             | 3.9                                    | 2.3                     | 43                   |
| Orimulsion      | 2 <sup>b</sup>           | 3           | 3.9                                    | 1.8                     | 58                   |
| Dry Bitumen     | 2                        | 3           | 3.7                                    | 2.5                     | 37                   |
| Pentane-Soluble | 2                        | 3           | 3.6                                    | 1.0                     | 74                   |
| Pentane-Soluble | 10                       | 3           | 3.6                                    | 2.8                     | 25                   |

<sup>a</sup> Ratio is based on the dry weight of bitumen contained in the Orimulsion.<sup>b</sup> Percent sulfur based on the dry weight of the bitumen contained in the Orimulsion.

Table 3. Hydrodesulfurization Reactions of Bitumen with Ni-U Oxide Catalysts.

| Catalyst              | Substrate      | Subst.:<br>Cat. Ratio | Time,<br>hr | Sulfur in<br>Substrate, <sup>a</sup><br>% | Sulfur in<br>Product,<br>% | Sulfur<br>Removed,<br>% |
|-----------------------|----------------|-----------------------|-------------|---|----------------------------|-------------------------|
| Ni-U Oxide            | Orimulsion     | 2 <sup>b</sup>        | 1           | 3.9                                       | 2.5                        | 38                      |
| Ni-U Oxide            | Dry<br>bitumen | 2                     | 3           | 3.7                                       | 2.4                        | 39                      |
| Ni-U Oxide + 5%<br>Mo | Dry<br>bitumen | 2                     | 3           | 3.7                                       | 2.4                        | 41                      |

<sup>a</sup> Ratio is based on the dry weight of bitumen contained in the Orimulsion.<sup>b</sup> Percent sulfur is based on the dry weight of the bitumen contained in the Orimulsion.